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16. ABSTRACT

Many of the key rate constants needed to predict rates of transformation and transport of organic chemicals in water and air can be estimated from structure-reactivity correlations (SRC) with reasonable accuracy. These rate constants can be coupled with environmental parameters such as pH or oxidant concentrations to provide estimates of rates of these processes under a variety of environmental conditions. SRC needed for zero-level testing are most abundant for hydrolysis, oxidation and sorption, and relatively scarce for photolysis and volatilization. Generalized SRC are readily used by non-expert, technically trained personnel whereas application of detailed SRC or linear free energy relationships (LFER) require expert knowledge in mechanistic chemical kinetics. An example is shown of the use of SRC methodology to estimate rate and equilibrium constants for a specific chemical.

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STRUCTURE REACTIVITY CORRELATIONS FOR ENVIRONMENTAL REACTIONS

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PREFACE

This report was prepared under the general guidance of the Project Officer, James Darr and the EPA Technical Monitor Asa Leifer. The report was prepared at SRI by Theodore Mill with assistance from Kirtland McCaleb (project leader). Valuable criticism was offered by Asa Leifer (EPA).

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SECTION 1

INTRODUCTION

Of the several hundred billion pounds of synthetic chemicals manufactured annually in this country, a significant amount enters the air, water, and soil, often at very low concentrations. Although biotic and abiotic processes rapidly transform some or most of these chemicals to simpler and harmless forms, a few chemicals persist, accumulate, and bioconcentrate, thereby affecting a wide variety of plant and animal life. In some cases human health is adversely affected as well.

The Toxic Substances Control Act was enacted to provide the EPA's Office of Toxic Substances (OTS) with the regulatory authority needed to control and minimize adverse effects of synthetic chemicals on the environment and on human health.

One of the important activities of OTS is to evaluate the possible environmental effects new chemicals may have if marketed and the effects existing chemicals may have because of their wide distribution, long persistence, high toxicity, or large production volumes. To facilitate this task, OTS has prepared a set of recommended test protocols for screening new chemicals for their environmental persistence and effects (Federal Register, 1979). The recommended protocols for fate are intended to provide data from simple laboratory kinetic or equilibrium measurements that can be used to evaluate the probable lifetime of a chemical in a specific environmental situation.

Despite the simplicity and low cost of the recommended test methods, their widespread adoption and use by chemical manufacturers poses two major problems. First, the total cost of performing most or all of the tests may be particularly burdensome for small manufacturing concerns that have limited staff and resources. These cost requirements may stifle innovation by small companies, particularly for potentially small-volume chemicals. Second, the large number of new chemicals to be tested each year (estimated at between 200 and 500) will generate a significant amount of kinetic and property data that must be evaluated by knowledgeable staff in OTS; the process of evaluating such quantities of data can lead to delays or, worse, inadequate assessments.

The test methods recommended by OTS reflect our present knowledge of the important processes that control transport and transformation of chemicals in the environment (Mill, 1979). Because some of the environmental processes have been well-studied in the laboratory for many years, a considerable body of empirical and theoretical knowledge is available from which to formulate structure-reactivity correlations (SRC); these correlations can then be used to relate molecular properties or structures to chemical or physical reactivity

in a specific process. Hydrolysis of simple esters is a good example of how the effect of changing the acid or alcohol structure can be systematized and used to predict the rate constant for a new structure (Euranto, 1969).

SRC are a valuable tool for predicting the probable range of reactivity for a new chemical structure in specific environmental processes; they are simple to use and can provide considerable savings in time and money for both EPA and industry if they are used carefully as a pre-testing tool to select only needed test protocols. This study was conducted to explore the scope of SRC and their potential value for predicting reactivity in environmental fate processes (zero-level screening).

SECTION 2

OBJECTIVES

The objectives of this study are to (1) evaluate the kinds and accuracy of existing SRC for environmental fate processes, (2) use these SRC to formulate some simple rules for including or excluding from testing specific types of molecular structures, and (3) indicate the accuracy of quantitative predictions of reactivity using SRC.

SECTION 3

RESULTS AND DISCUSSION

FATE ASSESSMENT BASED ON TEST PROTOCOLS

The current methodology for fate assessment may be summarized as follows; only the first two steps are now part of the proposed test program

- A chemical is screened in the laboratory to measure approximate rate or equilibrium constants for all processes that might control the transport or transformation of the chemical in the environment.
- The rate constants (or half-lives) are compared under selected environmental conditions to evaluate the dominant processes that control fate in specific environmental compartments.
- Additional detailed tests are performed for each dominant process (usually one to three) to evaluate rate constants or equilibrium constants over a range of environmental conditions.
- The important rate or equilibrium processes are integrated in a simple multicompartment computer model with environmental parameters and hydrologic or meterologic data. The model provides information on concentration as a function of both time and location in the environmental location of interest.

A more detailed discussion and application of this methodology is found in Smith et al. (1978).

ENVIRONMENTAL PROCESSES AND KINETIC RELATIONS

A detailed discussion of the kinetic or equilibrium processes thought to be important in the air, water, and soil is given in the recent paper by Mill (1979). Only a summary of that discussion is included here. Table 1 lists the processes that should be considered in any comprehensive review of environmental assessment. Each kinetic process listed in Table 1 can be formulated as a reaction and kinetic relation

$$C + X \longrightarrow \text{products} \tag{1}$$

$$-\text{Rate} = -d[C]/dt = k_n[C][X_n] \tag{2}$$

where C is the chemical, k_n is the specific rate constant for process n, and X_n is the chemical or biochemical species responsible for process n in the environment. X_n may be H^+, $HO\bullet$, soil organic content, or solar photon flux,

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Table 1 Environmental Processes and Properties

Process	Key Environmental Property[a,b]
Physical transport	
Meteorological transport	Wind velocity
Bio-uptake	Biomass
Sorption	Organic content of soil or sediments Mass loading of aquatic systems
Volatilization	Turbulence, evaporation rate, re-aeration coefficients, soil organic content
Run-off	Precipitation rate
Leaching	Adsorption coefficient
Fall out	Particulate concentration, Wind velocity
Chemical Transformation	
Photolysis	Solar irradiance, transmissivity of water or air
Oxidation	Concentrations of oxidants and retarders
Hydrolysis	pH, sediment or soil basicity or acidity
Reduction	Oxygen concentration, ferrous ion concentration and complexation state
Biological Transformation	
Biotransformation	Microorganism population and acclimation level

[a] At constant temperature.

[b] From Mill (1979).

as just a few examples.

Equilibrium processes for sorption are treated in a similar fashion

$$C + S \rightleftharpoons CS(\text{sorbed state}) \quad (3)$$

$$K_{oc} = [CS]/[C][S] \quad (4)$$

where S is the sediment/soil mass and K_{oc} is the measured value of K corrected for the organic content (Mill, 1979; Kenaga, 1979; Smith and Bomberger, 1979). Rate or equilibrium expressions such as (2) or (4) can be simplified to pseudo-first-order forms if $[X_n]$ is assumed to be constant during the measurement interval.

$$\text{Rate} = k_n[C][X_n] = k_n'[C] \quad (5)$$

Prediction of Rate and Equilibrium Constants

A systematic approach to predicting values of k_n or K_{oc} for new chemicals rests on the well-known fact that despite almost limitless diversity in structure, most organic chemicals share common reaction patterns and reactivites among like-structured chemicals; SRC are a way of explicitly recognizing and quantitating these similarities in reactivity for similar molecular structures. Thus, the estimation of rate constants is actually a two-part procedure

- Selection of environmental processes (see Table 1) applicable to a specific chemical structure using simple, qualitative SRC
- Estimation of kinetic rate constants for potentially important processes using quantitative estimation procedures such as linear free energy relationships (LFER) (Shorter and Chapman, 1972).

THE SCOPE AND APPLICATION OF SRC

Chemists generally use screening SRC implicitly to estimate what kinds of reactions a specific chemical will undergo, based on its molecular structure. Thus, for example, all organic chemists know that alcohols cannot hydrolyze, alkanes cannot absorb sunlight, but that acyl halides hydrolyze very rapidly; fewer chemists could instintively classify thiadiazoles or dialkylaromatic carbamates as unreactive in hydrolysis or photolysis, and fewer still would be able to estimate whether hindered aromatic phenols or amines will oxidize in the dark. Thus, screening SRC covers a range of easy-to-difficult classifications of reactivities, but in each case only a yes or no decision is required.

To predict how fast or significant a particular reaction will be for a particular chemical structure chemists use quantitative SRC such as LFER. For example, the sensitivity of ionization of phenylacetic acids in water at 25°C to substituents is expressed as the $\sigma\rho$ relation (Wells, 1963)

$$\log K\ (XPhCH_2COOH) = \log K(PhCH_2COOH) + (0.562 \pm 0.039)\sigma \quad (6)$$

Equation (6) is an example of LFER that link kinetic and thermodynamic parameters to molecular structure in a quantitative framework. Both screening SRC and LFER are useful for predicting environmental fate and persistence from information about molecular structure and properties, but often only the qualitative SRC is needed to select test protocols for a particular chemical. This is because of the several competing processes that might control the persistence of a chemical in air, water or soil, only the one or two fastest processes will control fate and the other slower ones will have little or no influence on fate. Thus, if screening SRC predicts that processes A and B will be faster than processes C, D, and E by a factor of 10 or more, it matters little if the rate factor is actually 10 or 10,000 since the decision to exclude tests for processes C, D, and E is a valid one for all rate factors larger than 10. Usually the confidence in these predictions increases with an increase in the rate factors.

For competing processes A and B, LFER may be usefully applied to predict more quantitatively the values of k_A and k_B. Unfortunately, application of LFER to predicting a new rate constant from a set of measured ones is subject to uncertainty and limitations, as discussed below.

THE SCOPE AND APPLICATION OF LFER

LFER relate rates contants and structural parameters through a general form, linear in log k (thus linear in $\Delta F^{\ddagger}$)

$$\log k_X = \log k_0 + \alpha\beta \quad (7)$$

where k_X is the unknown, rate constant k_0 is known, and α and β are reaction, structure, or solvent parameters. The Hammett, Bronsted, Taft, Swain, Grunwald-Winstein, and other LFER equations are of this form. The term free energy implies a more fundamental thermodynamic foundation than is justified; all these correlations are almost entirely empirical in origin and elaboration.

The range of reactivities that can be correlated with equation (7) is indeed impressive, with some changes in k_X ranging over 14 log units. These are exceptional ranges, however, and most LFER cover 1 or 2 log units in rate constant (Wells, 1963; Shorter and Chapman, 1972).

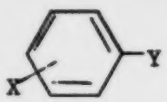
Hammett Equation

One of the best known and most widely used LFER is the Hammett equation originally developed for correlating the acidity of substituted benzoic acids.

$$\log k_X = \log k_0 + \sigma\rho \quad (8)$$

In equation (8):

(1) k_X and k_0 are rate or equilibrium constants for reaction of an aromatic structure at a single temperature



(2) X is a m- or p-substituent in the ring; Y is the reaction center.
(3) k_X and k_0 refer to the X-substituent and H-substituent (parent), respectively
(4) σ is the substituent constant characteristic of the substituent alone and independent of the type of reaction, but is a function of temperature and solvent.
(5) ρ is the reaction constant characteristic of a specific reaction and transition state.

Many modifications have been made to the Hammett equation to extend its range of applicability; extensive reviews of LFER by Wells (1962) and Shorter and Chapman (1972) are recommended for details. For this discussion we need to focus on the two essential but limiting features of LFER: (1) the requirement for a simple and constant reaction (similar transition states) for a valid correlation, and (2) the largely empirical nature of LFER, which requires an extensive experimental data set to develop the reaction constants needed for further prediction. These features restrict the usefulness of LFER for predicting new rate constants even though this objective was one of the mainsprings for development of LFER.

Exner (1972) has discussed the range of validity of LFER, particularly equation (8), in some detail. Many deviations from the LFER occur because the reaction mechanism changes with the change in substituent. Examples are shown in Exner's paper (see Figures 1.1-1.9). The application of LFER to a particular reaction is often used as a sensitive criterion for detecting similarities and differences in transition states for a similar group of chemical structures. If LFER is used instead to predict a value for k_X, then there must be some a priori basis for knowing which particular value of ρ (or the corresponding constant in another LFER) to choose for a particular reaction. For simple, closely analogous reactions (e.g., ester hydrolysis, H-atom transfer from aromatics), selection of correct values of ρ is generally straightforward; however, for some chemical structures and reactions, selection of the correct value of ρ may prove very difficult if not impossible. Two examples (from Exner, 1972) will illustrate the point: (1) in a series of substituted cumyl chlorides, solvolysis of p-nitrocumyl chloride has a measured rate constant almost one hundred times as fast as that predicted from the (good) correlation equation based on m-substituents and nonconjugating p-substituents, and (2) acid-catalyzed addition of water to carbodiimides shows excellent correlation for 12 substituents; however, for 3-Me_2N, the deviation from the line corresponds to a factor of 10, and for 3-NO_2, the deviation corresponds (approximately) to a factor of 50 in rate. Failure of the equation apparently results from a change in mechanism.

Development of a useful LFER does require a data base from which to derive a best value of ρ (or other reaction constants). A priori thermodynamic and quantum mechanical procedures for calculating ρ from first principals have been tried with only minimal success. For the immediate future, investigators must continue to rely on careful experimental studies to extend the usefulness of LFER to environmental problems; where no data base exists, application of LFER probably is imprudent.

Precision of LFER

Values of ρ, α, or other reaction constants are typically evaluated by fitting data on log k, log k_X, or log K_A versus substituent constants, to a regression equation using simple linear least squares methods. Error bounds or confidence limits on ρ or α can then be calculated (Wells, 1963). Several interesting points arise from examining the data of Wells. Most correlation coefficients reported for r are > 0.98 [standard deviations typically are less than 5%], but few reaction series cited contain more than eight substituents. Exner has proposed that a better measure of the usefulness of a LFER than r is ϕ:

$$\phi = [n(1-r^2)/(n-2)]^{\frac{1}{2}} \qquad (9)$$

Applying equation (9) to a good data set where r = 0.998 for the Hammett equation and n = 5 (Wells, 1963) gives

$$\phi = (5(1-0.998)/3)^{\frac{1}{2}} = 0.08$$

In this case, use of the Hammett equation for calculating log k_X will give a mean deviation only 8%, as large as would be obtained by assuming that substituents have no effect (ρ = 0). However, for another example where r = 0.96 and n = 5, ϕ = 0.36; in this case use of the Hammett equation gives a mean deviation which is 36% as large as would be obtained by assuming that ρ = 0. If more data points were available such that n = 10, then ϕ = 0.31; if n = 25, then ϕ = 0.29.

Table 2, from Exner (1972), summarizes values of Hammett substituent constants σ for meta and para substituents. By definition H is zero. Other substituents may have positive ρ or negative values of ρ ranging from +1.9 for $-N_2^+$ to -0.66 for p-NH_2. The range of values for k_X covered by these substituents is almost 400 if ρ = 1.00.

Values of σ in Table 2 seem best suited for use in reactions in which the transition states have no strong local charge development. Aromatic reactions in which significant localized charges develop in the transition states are better correlated by parallel substituent sets designated σ^+ or σ^-. In general, correlations of polar reactions with these substituents are not as extensive nor as good as those with σ.

Perhaps the main point to be emphasized is that statistical tests alone cannot be used to judge whether a new chemical structure will fall on a particular correlation line; some insight into the probable reaction mechanism is a necessary requirement to using LFER as a reliable predictive tool.

TABLE 2. SELECTED VALUES OF HAMMETT σ VALUES[a]

Substituent	σ_m[b]	σ_p[b]
H	0.00	0.00
Me,Et,i-Pr	-0.04 to 0.07	-0.14 to 0.17
t-Bu	0 to -0.12	-0.18 to -0.20
C≡CH	0.20	0.23
Ph	0.06 to 0.22	-0.01 to 0.02
CH_2CN	0.16	0.01 to 0.18
CF_3	0.42 to 0.43	0.54 to 0.55
CCl_3	0.40	0.46
CN	0.56 to 0.68	0.63 to 0.69
CHO	0.36	0.22 to 0.43
C(O)Me	0.31 to 0.38	0.44 to 0.52
$C(O)NH_2$	0.28	0.38
CO_2H	0.35 to 0.37	0.26 to 0.45
CO_2R	0.36 to 0.40	0.43 to 0.52
NH_2	0.00to -0.16	-0.57 to -0.66
N_3	0.27	0.15
NO_2	0.70 to 0.71*	0.78 to 0.80
OH	0.00 to 0.12	-0.36 to -0.37
OMe	0.12	-0.27
OC(O)Me	0.26 to 0.39	0.16 to 0.31
SH	0.25	0.15
SO_2NH_2	0.46 to 0.53	0.57 to 0.62
F	0.34	0.06
Cl	0.37	0.23
Br	0.39	0.23
I	0.35	0.18 to 0.28
NMe_3^+	0.88 to 0.99	0.82 to 0.96
N_2^+	1.8	1.9
CO_2^-	-0.1 to 0.10	-0.05 to 0.13
SO_3^-	0.05 to 0.31	0.09 to 0.38

[a] From Exner (1972).
[b] Range, where given, indicates extremes of values listed.

LFER for reactions of aliphatic structures have been developed by Taft and reviewed in detail by Shorter (1972). In general, the Taft equation and its elaborations do not correlate reactivity in aliphatic systems as well as the simple Hammett equation does for aromatic systems and successful application of LFER to aliphatic chemicals requires considerable insight into the mechanisms of their reaction.

Another form of the Hammett equation is used to describe SRC for substitution reactions in which the stability of the leaving group controls rate.

$$A^- + BX \rightleftharpoons AB\bar{X} \longrightarrow AB + X^-$$

$$\log k_X = \log k_0 + \rho \log K_X \qquad (10)$$

In this form of the equation, log K_X measures the stability of the anion relative to its conjugate acid in water or another basic solvent.

$$H_2O + XH \rightleftharpoons X^- + H_3O^+ \qquad (11)$$

Examples of the application of equation (11) are given in the section on hydrolysis.

Bronsted Catalysis Equation

Structural changes in the reactant that effects a transformation at a reaction center can be successfully correlated by the Bronsted equation; in its simplest form, this equation relates acid or base strength to catalytic activity in reactions involving general catalysis.

Because hydrolysis in natural waters usually involves only specific acid (H_3O^+) or base (OH^-) catalysis, the Bronsted equation is little used in environmental estimates. Correlation of pK_A or log k_A and rate constant, cited above [equation (11)], is sometimes referred to as a Bronsted correlation (Williams, 1972).

Use of SRC and LFER for Environmental Processes

Table 1 lists the processes believed to control transport and transformation in the environment. Some physical transport processes, such as volatilization, can be related to thermodynamic properties of the chemical in dilute solution and are therefore amenable to correlation by LFER. Other processes, such as sorption to sediment, particulate, or biomass, can be correlated most readily with solubility or partitioning between organic and aqueous or vapor phases. The relationship between molecular structure and thermodynamic or kinetic parameters is less clear for these latter processes.

Biotransformations are always mediated by enzymes through one or more equilibrium processes usually coupled to an irreversible bond-breaking or bond-making step on the enzyme. In principle, the processes are susceptible to treatment by LFER; in practice, few such relationships have been successful

owing to the complexity of the overall process and the lack of detailed understanding of the chemistry of individual steps. Some correlations of microbial and chemical rate constants are reported by Wolfe et al. (1979).

A number of chemical transformations in the environment can be separated into discrete elementary steps characterized by simple kinetic relationships, many of which can be examined in detail. Therefore, many correlations can be made between structural reactivity with reasonable assurance of their applicability to environmental situations. For these reasons we have emphasized the use of SRC and LFER for chemical transformations in this report.

Chemical Transformations

Table 3 lists four basic types of chemical processes that occur in the environment and the environmental agents that effect these processes.

TABLE 3. ENVIRONMENTAL CHEMICAL PROCESSES

Process	Agent, Property
Hydrolysis	H_2O, H_3O^+, OH^-, trace metals sediment
Photolysis	Solar irradiance, transmissivity of water or air
Oxidation	$HO\bullet$, $RO_2\bullet$, $^1O_2$, O_3, $RO\bullet$
Reduction	Fe^{2+}

For many of the processes listed in Table 3 we can formulate simple kinetic relationships of the form

$$\text{Rate} = k_n[C][P_n] \qquad (12)$$

where k_n is the rate constant for the n-th process, [C] is the concentration of chemical and $[P_n]$ is the concentration of environmental agent or property of the n-th process. Prediction of the rates of many environmental processes requires only prediction or measurement of the rate constant k_n because concentrations of hydrolytic, oxidative and solar agents are now known for a variety of environmental situations (Mill, 1979). The following sections will examine the detailed processes and usefulness of SRC for predicting rate constants.

Hydrolysis

Hydrolysis or organic compounds usually results in introduction of a hydroxyl function (-OH) into a chemical, most commonly with the loss of a leaving group (-X).

$$RX + H_2O \longrightarrow ROH + HX \qquad (13)$$

$$R\text{-}\overset{O}{\overset{\|}{C}}\text{-}X + H_2O \longrightarrow R\text{-}\overset{O}{\overset{\|}{C}}\text{-}OH + HX \qquad (14)$$

In water, the reaction is catalyzed mainly by hydronium and hydroxyl ions, but in moist soil, loosely complexed metal ions such as copper or calcium may also be important catalysts for certain types of chemical structures. Sorption of the chemical may also increase its reactivity toward H^+ or HO^-.

The general rate equation for hydrolysis in water is

$$R_h = k_h[C] = k_A[H^+][C] + k_B[OH^-][C] + k_N'[H_2O][C] \qquad (15)$$

where k_h is the measured first-order rate constant at a given pH. The last term is the neutral reaction with water (second-order rate constant k_N'), and in water it can be expressed as a pseudo-first-order rate constant k_N.

This equation can be modified to account for the incursion of bound or free metal-ion catalysis in soil or sediments by including one or more terms for the form

$$k_M k_A[M]_T/(k_A + [H^+]) \qquad (16)$$

where k_M is the metal-ion catalysis constant, $[M]_T$ is the total metal ion concentration, and k_A is the equilibrium constant for dissociation of the hydrated ion complex. Since a metal may be complexed in soil in several ways, the descriptors needed for the complete rate equation could be quite complex.

Equation (15) shows that the total rate of hydrolysis in water is pH-dependent unless k_A and $k_B = 0$.

Mabey and Mill (1978) have recently reviewed kinetic data for hydrolysis of a variety of organic chemicals in aquatic systems and have reviewed the chemical characteristics of most freshwater systems. These data have been used in turn to calculate persistence (half-lives) of these same chemicals at 25° and at pH 7 in freshwater. Predictive test methods (screening and detailed) for hydrolysis to develop the essential kinetic data: k_h, k_A, k_N, k_B, and their temperature dependence (Arrhenius equation) have been prepared recently by SRI.

A variety of hydrolysis reactions have been observed on soils and sediments. In some cases, rates were markedly accelerated compared to bulk solution, but detailed understanding of mechanisms is limited and structure-reactivity relationships appear to be available for only a few compounds.

The review of Mabey and Mill (1978) is a useful point of departure for summarizing the SRC for hydrolysis in pure or natural water where only H_2OHO^- and H^+ are important catalytic agents. Organic chemicals can hydrolyze by a variety of processes including both solvolytic and substitution mechanisms catalyzed by H_3O^+ and OH^-. We can narrow the scope of the enquiry by restricting our interests to reactions proceeding at pH 7 and 25°C. General and detailed effects of structure on hydrolytic reactivity, as measured by the half-life at pH 7, are summarized in Tables 4 through 11. In some cases half-lives are expressed only as > or < 1 year or some multiple thereof.* By this classification, one can quickly differentiate the reactive from the unreactive chemical structures. For some classes, the information on LFER can be used to make detailed estimates of reactivity based on structure.

Table 12 provides an summary of hydrolyzable chemical structures that will be expected to persist in water for significantly more than a year at pH 7 and 25°C. These classes of chemicals probably need not be screened in the laboratory for hydrolysis using the current screening tests because these tests are designed to estimate reliably only those half-lives of a few hours to a few months; longer half-lives are not well-defined by the test method (Federal Reg., 1979) and, indeed, current assessment procedures generally focus only on chemicals that exhibit loss rates of days to weeks.

Photochemistry

Measurement Methods

The cutoff for the solar spectrum by the upper atmosphere is at about 290 nm; only absorption of photons by a chemical at this or longer wavelengths can result in direct photochemical transformations. Direct absorption of sunlight may result in cleavage of bonds, dimerization, oxidation, hydrolysis, or rearrangement. No simple selection rules are available to predict the specific chemical process that may occur, although some useful generalizations have been found (Calvert and Pitts, 1967; Turro, 1978).

Quantitative aspects of direct photolysis in water, on soil surfaces, or in the atmosphere have the same general kinetic relationships. The rate of absorption of light, I_A (rate constant k_a), by a chemical at one wavelength is determined by ε_λ, the molar absorbance; I_λ, the intensity of the incident light at wavelength λ; and [C], the concentration of chemical. At low concentrations of C where only a small percentage of the light is absorbed

$$I_{A(\lambda)} = \varepsilon I_\lambda [C] = k_{a(\lambda)} [C] \qquad (17)$$

The rate of direct photolysis of a chemical at wavelength λ is obtained by multiplying $k_{a(\lambda)}$ by the quantum yield ϕ_λ, which is the efficiency for

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*This time limit is somewhat arbitrary but corresponds to the limits on estimation of rate constants using EPA screening test protocols.

TABLE 4. HYDROLYSIS OF ESTERS AT pH 7 AND 25°C[a,b]

$R_1C(O)OR_2$[c]		Half-life (yr)
General SRC		
R_1	R_2	
Al	Al	> 1 (2-100)
Al	Ar	<< 1
H	Al	< 1
Al	allyl	< 1
Ar	Al	>> 1
Al	Ar	?
XCH_2, X_2CH	Al (X = Cl, F)	< 1
Allyl	Al	> 1
LFER[d]		
Acid Catalysis		
$XArC(O)OEt$		$\rho = -0.2$
$MeC(O)OAr$		$\rho = 0.11$
Base Catalysis		
$XArC(O)OAl$		$\rho = 2.0$
Leaving Group pK_a		
$AlC(O)OArX$: When pK_A of HOArX is less than 8, $t_{1/2}$ for hydrolysis is < 1 yr		
Steric Effects		
$MeC(O)OAl$: As bulk of Al increases from Me to t-Bu, $t_{1/2}$ increases by a factor of almost 100.		

[a] From Tables 4.8 and 4.9 in Mabey and Mill (1978).

[b] k_B is the dominant term in k_h.

[c] Al = alkyl, ar = aromatic.

[d] Euranto (1969).

TABLE 5. HYDROLYSIS OF AMIDES AT pH 7 AND 25°C[a]

$R_1C(O)NR_2R_3$[b]			Half-life (yr)
R_1	R_2	R_3	
Al	H	H	>> 1
XAl	H	H	> or >> 1 for X = MeO, Cl, Br
Cl_2CH	H	H	<< 1
Cl_3C	H	H	
Al	Al	H	>> 1[c]
XAr	H	H	>> 1[c], X = H to NO_2
XAr	Al	H	>>> 1[c], X = Me to Pr

[a]From Table 4.10 in Mabey and Mill (1978).

[b]From footnote c, Table 4.

[c]Estimated from H_3O^+-catalyzed rate only at 50-100°C.

TABLE 6. HYDROLYSIS OF NITRILES AT 25°C[a]

RCN	Half-life (yr)
Al(Me, Et, Pr)	> 100[c]
$ArCH_2$	> 1000[d]
Ar_2CH	> 10^4[d]
$NCCH_2$	> 10^4[e]

[a]At pH 9; slower at lower pH.

[b]Footnote c, Table 4.

[c]Widequist.

[d]Zavaoianu (1968).

[e]Bloch et al. (1973).

TABLE 7. HYDROLYSIS OF ACYL CHLORIDES AT 25°C[a]

RC(O)Cl	Half-life[b]
General	
Me	< 10 sec
Me_3C	< 40 sec
EtO	10 hr
Me_2N	4 min
p- or m-XPh (X = NO_2, Br, MeO, Me)	1-12 min
LFER	
XPhC(O)Cl	ρ = 1.57-2.0[c,d]

[a]Kiniven (1972).
[b]Based on first-order rate constant for reaction with water.
[c]Kiniven
[d]Hudson et al. (1970).

TABLE 8. HYDROLYSIS OF CARBAMATES AT pH 7 AND 25°C

$R_1OC(O)NR_2R_3$[a]			Half-life, yr
General SR[b]			
R_1	R_2	R_3	
Al	Al	Al	>> 1
Al	Ar	Ar	>> 1
Al	Ar	H	>> 1
Al	Al	H	>> 1
Ar	Ar	H	< 1
Ar	Al	H	< 1
Ar	Ar	Al	>> 1
Ar	Al	Al	>> 1
R_3N^+	Al	Al	∿ 1
R_3N^+	Al	H	∿ 1
X_nCH_{3-n}	Ar	H	1-150
		X = Cl or F	

LFER

XArOC(O)N(Ar)H:	$\log k_X = 15.2-1.34\ pK_a$[c]
	$\log k_X = 13.6-1.15\ pK_a$[d]
	$\log k_X = 2.04 + 2.87\sigma$[c]
XArOC(O)N(Ar)Me:	$\log k_X = -1.3-0.26\ pK_a$[d]
XArOC(O)N(Me)H:	$t_{1/2}$ < 5 yr if pK_a < 10 (at pH 8)
XArOC(O)N(Me)Al:	$t_{1/2}$ > 1 yr for all values of pK_a (at pH 8)
XArOC(O)N(Ar)H:	$t_{1/2}$ < 0.5 yr if pK_a < 12 (at pH 8)

[a] Footnote c, Table 4.

[b] From Table 4.5 in Mabey and Mill (1978).

[c] Williams (1972).

[d] Wolfe et al. (1978).

TABLE 9. HYDROLYSIS OF ALKYL HALIDES AT pH 7 AND 25°C[a]

RX			
R[b]	X		Half-life (yr)
Al	F		> 1
Al	Cl, Br, I		< 1
Allyl	Cl, Br, I		<< 1
$ArCH_2$	Cl, Br, I		<< 1
$AlOCH_2$	Cl		< 1 hr
CH_{4-n}	Cl, Br	n = 2-4	>> 1

[a]From Table 4.1 Mabey and Mill (1978).

[b]Footnote c, Table 4.

TABLE 10. HYDROLYSIS OF PHOSPHORIC ACID ESTERS AND HALIDES AT pH 7 AND 25°C[a]

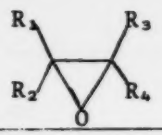
$R_1P(O)R_2R_3$			
R_1	R_2	R_3[b]	Half-life (yr)
Phosphonates $R_1P(O)(OR)_2$			
Al	AlO	AlO	>> 1
Ar	AlO	AlO	>> 1
Phosphates $(RO)_3P(O)$			
AlO	AlO	AlO (Al = Me or Et)	∿ 1
ArO	ArO	ArO	∿ 1
p-NO_2ArO	p-NO_2ArO	p-NO_2ArO	<< 1
Phosphonohalidates $R_2P(O)X$			
Al	Al	F	<< 1
AlO	AlO	F	< 1
Al	AlO	F	> 1
Al_2N	Al_2N	Cl	<< 1

[a]From Tables 4.13-4.17, Mabey and Mill (1978).

[b]Footnote c, Table 4.

TABLE 11. HYDROLYSIS OF EPOXIDES, IMIDES, AND CYCLIC ESTERS AT pH 7 AND 25°C

Epoxides and Imides[a]



R_1	R_2	R_3	R_4	Half-life (day)
H	H	H	H	12
Me	H	H	H	14
Me	Me	H	H	4
XCH_2	H	H	H	8-28
XCH_2	Me	H	H	16
	X = HO, Cl, Br			
Me	H	Me	H	16
H	H	H	H	$\lesssim$ 1 yr[c]

Cyclic Esters[b]

$R_1C(O)OR_2$ or $R_1OS(O)_nOR_2$	
β-Lactones	<< 1 yr
β-Sultones	<< 1 yr
Sulfates	< 1 yr

[a]From Table 4.7, Mabey and Mill (1978).

[b]From Table 4.18, Mabey and Mill (1978).

[c]Ethyleneimine.

TABLE 12. SUMMARY OF CHEMICALS PERSISTENT TO HYDROLYSIS: HALF-LIVES > 1 YR AT 25°C AND pH 7

Category	Persistent Chemicals
Esters, $R_1C(O)OR_2$	All Al esters of Al, Ar, or allylic acids
Amides, $R_1C(O)NR_2R_3$	All amides where R_1 - R_3 are Al or Ar; only amides with halogenated alkyl R_1 hydrolyze rapidly.
Nitriles RCN	All aliphatic or aromatic nitriles
Acyl chlorides RC(O)Cl	No acyl chlorides
Carbamates $R_1OC(O)NR_2R_3$	All carbamates having only Al or Ar on N and O
Alkyl halides RX	All AlF and polychloro- or polybromo-methanes
Phosphorous acid esters and halides $R_1P(O)R_2R_3$	All esters where R_1 is Al or Ar and R_2 and R_3 are AlO or ArO (Phosphonates); no esters where R_1 - R_3 are AlO or ArO (phosphates); only esters where R_1 and R_2 are Al_2N and R_3 is F (phosphono-halidates).
Epoxides, lactones, sultones	Only hindered, bicyclic epoxides; no simple lactones or sultones

converting the adsorbed light into chemical reaction, measured as the ratio of moles of substrate transformed to einsteins of photons absorbed. Thus at a single wavelength, λ

$$k_{a(\lambda)}\phi_\lambda[C] = k_{p(\lambda)}[C] \tag{18}$$

where

$$k_{p(\lambda)} = k_{a(\lambda)}\phi_\lambda \tag{19}$$

The simplest and most direct method of using laboratory experiments to estimate environmental photolysis rates in the field is to expose an aqueous solution, a vapor phase sample, or a thin surface layer of a chemical to outdoor sunlight and monitor its rate of disappearance. At the same time photolysis of another chemical having a well-characterized quantum yield and similar absorption spectrum should be carried out. This method will take into account variations in sunlight intensity but avoids the need for determining the detailed spectrum or the quantum yield for the chemical.

Another method for estimating environmental photolysis rates is based on laboratory measurements of ϕ at a single wavelength ; average sunlight intensity (I_λ) data are available in the literature as a function of time of day, season, and latitude (Mabey et al., 1979 ; Zepp and Cline, 1977).

Since k_p is equal to the product of k_a and the quantum yield ϕ, and since ϕ generally does not vary significantly with wavelength, the rate constant in sunlight $k_{p(S)}$ is

$$k_{p(S)} = \phi\Sigma_\lambda\varepsilon_\lambda I_\lambda \tag{20}$$

and the half-life in sunlight is

$$(t_{\frac{1}{2}})_{(S)} = \frac{\ln 2}{k_{p(S)}} \tag{21}$$

Both computer and hand methods are available to sum the products of $\varepsilon_\lambda I_\lambda$ over a wavelength range, and give a plot of the half-life of the chemical toward photolysis in water or air as a function of the month of the year and latitude (Mabey et al., 1979; Hendry et al., 1979).

Comparisons were made at SRI between measured and calculated half-lives for direct photolysis in sunlight of eight chemicals dissolved in water using procedures described above; the comparisons gave excellent agreement, usually within a factor of 2 (Smith et al., 1978).

Predictive Methodology

Equation (20) may be used to calculate an upper limit for k_p by assuming $\phi = 1$. This method is recommended as a screening tool since if the rate constant is small compared to rate constants for other competing

environmental processes, no additional photolysis measurements are needed.

The foregoing discussion and equation (20) show that only the intensity ε and quantum yield ϕ at wavelengths in the solar spectrum are needed to predict quite accurately the photochemical loss rate of a chemical in sunlight. For the prediction, no information is needed on the actual chemical reaction occurring. Application of SRC to photochemical reactions must then address two separate problems: how does structure affect ε_λ and ϕ_λ?

There is no simple or succinct answer to this question. However, some generalizations are possible because of a large body of empirical data organized on the basis of a slim theoretical framework (Calvert and Pitts (1967), Baltrop and Coyle (1975), Turro (1978).

Spectral Properties

Equation (20) shows that the total rate constant for loss of a chemical by solar radiation is related to the sum of all absorption bands. Thus, a chemical with a very weak tailing absorption spectrum extending into the solar region for 50-100 nm could largely photolyze in less than a year if the quantum yield is reasonably high.* For this reason, conventional criteria for weak or strong absorption spectra are not very useful. Table 13 lists classes of chemicals that exhibit significant light absorption beyond 290 nm.

The list in Table 13 is by no means inclusive, but, as a general rule, carbon singly bonded to carbon or to other more electro-negative elements absorbs only weakly or not at all in the solar spectrum. Carbon multiply bonded with electronegative elements does exhibit weak-to-strong absorption between 290-350 nm, and conjugated structures absorb more strongly and at higher wavelengths. Singly bonded heteroatoms such as O-O, S-O, and N-N also exhibit weak-to-moderate absorption bands in the solar region. These familiar generalizations provide the basis only for a crude separation of chemical structures into solar-active and solar-inactive categories. More detailed SRC are difficult to formulate at this time because of the current limited knowledge of the photophysics of excited states (Turro, 1978).

Energetics of Photoprocesses

The energy of light photons in the solar region decreases from 98.6 kcal/einstein at 290 nm to 35.7 kcal/einstein at 800 nm.† The kinds of

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*A hypothetical chemical with a constant absorbance ε of 0.1 M^{-1} cm^{-1} extending from 290 to 350 nm will have a $t_{\frac{1}{2}}$ of 160 days if ϕ = 0.1, and a $t_{\frac{1}{2}}$ of 16 days if ϕ = 1.0 (Mabey et al., 1978).

†The relation between energy in kcal/einstein and wavelength in nm is

$$\text{photon energy} = 28590/\lambda$$

TABLE 13. APPROXIMATE ABSORPTION REGIONS FOR ORGANIC MOLECULES

Class	Example	Region nm	Reference
Aliphatics[c]			
hydrocarbons	$n\text{-}C_4H_{10}$	120-170	a
fluorides, chlorides bromides	$CHBr_3$, $CHCl_3$	180-260	a, b
iodides	C_3H_7I	180-320	b
ethers, alcohols	C_2H_5OH, $C_2H_5OC_2H_5$	150-200	a
aldehydes	CH_3CHO	240-340	a
ketones	$C_2H_5C(O)CH_3$	240-320	a, b
acids	$CH_3C(O)O$	200-230	a, b
esters	$CH_3C(O)OCH_3$	200-240	a
amides	$C_2H_5C(O)NHt_2$	180-220	a, b
amines	$(C_2H_5)_3N$	180-240	a, b
azines	$(CH_3)_2C=N-N=C(CH_3)_2$	200-290	b
azo	$CH_3-N=N-CH_3$	200-230, 320-400	a
nitro	CH_3NO_2	200-220, 260-320	a, b
nitroso	$(CH_3)_3CNO$	200-300, 540-740	a
nitrite	$(CH_3)_3CONO$	200-240, 320-400	a, b
nitrate	$C_2H_5ONO_2$	200-300	a
sulfide	$C_2H_5SC_2H_5$	200-220	a, b
disulfide	CH_3SSCH_3	200-240	a, b
Non-conjugated[c] Olefinics and Acetylenes			
hydrocarbons	$(CH_3)_2C=C(CH_3)_2$	170-240	a, b
aldehydes	$CH_2=CHCHO$	200-250, 290-400	b
ketones	$CH_3CH=CH-C(O)CH_3$	200-240, 260-330	b
nitro	$CH_3C(NO_2)=C(CH_3)_2$	180-380	b

[a]Calvert and Pitts (1967).

[b]Perkampus (1971).

[c]From Hendry and Kenley (1979).

TABLE 13 (concluded)

Class	Example	Region nm	Reference
Aromatics			
benzene	Benzene	200-280	a
alkylbenzenes	Toluene	200- > 280	a
halobenzenes	Cl- or Br-benzene	200-280	a
nitrobenzenes	Nitrobenzene	200-330	a
	Trinitroluene	200-450	d
aminobenzenes	Aniline	200-3300	a
azobenzene	Azobenzene	< 200- > 500	a
phenols	Phenol	200-305	a
vinylbenzenes	Styrene	200-300	a
	Stilbene	200-330	a
acids	4-nitrostilbene	200-390	a
	Benzoic acid	200-300	a
carbonyls	Benzaldehyde	200-375	a
	Benzophenone	200-410	a
polycyclic aromatics	Napthalene	200-325	a
	Anthracene	200- > 400	a
	Phenanthrene	200-380	
	Benzo[a]pyrene	200-410	e
heteroaromatics	Quinoline	200-360	e
	Benzoquinoline	200-380	e
	9H-Carbazole	200-390	e
	Benzo[b]thiophene	200-312	e

[d]Spanggord et al (1979).

[e]Smith et al (1978).

photoprocesses that can occur at specific wavelengths are therefore limited by the energy available from absorption of one photon per molecule. Simple homolysis reactions ($XY \rightarrow X\bullet + Y\bullet$) are limited by bond dissociation energies of different bonds which vary from 112 kcal/mole for Ph-H to 38 kcal/mole for RO-OR (Benson, 1976). Thus, a photoprocess that leads to homolytic bond cleavage can occur efficiently only below the wavelength limit imposed by the bond dissociation energy. For example, photocleavage of the C-Cl bond (83 kcal/mole) in $CH_3C(O)Cl$ can occur only at wavelengths below 346 nm.

These comments also apply to concerted processes; however, the energetics of the concerted process are very difficult to predict except that the activation energy is always lower than for the nonconcerted process involving the same bond breaking and making steps. Thresholds for concerted reactions will therefore be at longer wavelengths.

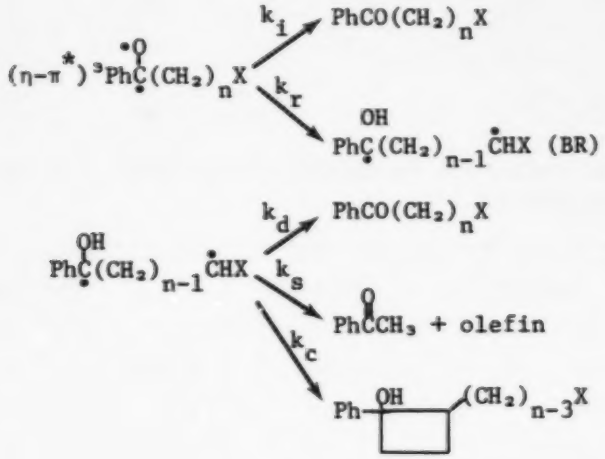
Quantum Yield Estimates

The simplest assumptions one can make about a photochemical quantum yield is that it is zero or one over the entire solar spectrum. In the former case, no additional testing is needed; in the latter case, k_p, calculated from equation (20), is the upper limit for the rate constant.

More accurate estimates of ϕ_λ may be possible because SRC exist for the chemicals of interest or because a published value at one wavelength is available. In either case application of equation (20) explicitly assumes that ϕ_λ is constant over the range of wavelengths where light is absorbed. This assumption is a reasonably good one providing the absorbed photon energy is not below the threshold energy needed to effect the reaction (see previous section). In this case ϕ will quickly go to zero as λ increases. Turro et al. (1978) have discussed the exceptional cases where ϕ or products are wavelength-dependent in solution.

Photochemists are particularly interested in studying efficient reactions that produce only a few products, usually in organic solvents or in the gas phase and in the absence of oxygen, which is an efficient quencher of many photoprocesses. As a result, published quantum yield data on the bulk of organic photoreactions provide, at best, only rough estimates of quantum yields in aerated water or air.

SRC for product quantum yields in organic photochemistry are very limited both by the number of measurements and by the complex photophysics associated with even simple photolysis processes. The best studied processes are those of ketones. A simplified photokinetic scheme for arylalkyl ketones is shown below. The Type II process involves cleavage to acetophenone and olefin via a biradical (BR). The competing pathways controlling the fate of the BR also determine the value of ϕ_{II}



$$\phi_{II} = \phi_{BR}\phi_P$$

$$\phi_{II} = \left(\frac{k_r}{k_r + k_i}\right)\left(\frac{k_s}{k_s + k_c + k_d}\right)$$

Polar solvents such as alcohols (and presumably water) eliminate the back reaction (k_d) and in most cases ϕ becomes 1.0. In organic solvents, however, ϕ_{II} is generally closer to 0.3-0.4 owing to competitive reversion to ketone (k_d) (Wagner and Kemppainen, 1968; Turro, 1978).

Substituents on the aromatic ring such as p-MeO or p-NO_2 generally have small effects on ϕ_{II} except where the substituent affects the relative energy levels of the reactive $(n\text{-}\Pi^*)^3$ and less reactive $(\Pi\text{-}\Pi^*)^3$ states. Phase effects on ketone photolysis may be significant if α-cleavage is the major process because the solvent cage promotes recombination rather than dissociation.

$$RCOR' \overset{h\nu}{\rightleftharpoons} [R\dot{C}O + R'\bullet]_{cage} \longrightarrow R\dot{C}O + R\bullet'$$

Acetone exhibits a marked increase in cleavage rate on going from the liquid to the vapor phase, but long-chain ketones, which can also cleave via a Type II process, may exhibit smaller phase effects (Calvert and Pitts, 1967). Table 14 summarizes quantum yield data for α- and β-cleavage of ketones and indicates the magnitude of substituent, solvent, and phase effects on these processes.

The complex photophysics may be additionally complicated by the presence of oxygen. The effect of oxygen on photolytic processes is difficult to predict, but some generalizations from other studies indicate that in the presence of oxygen two processes can occur: (1) quenching by energy transfer to give ground state species and either $^3O_2$ or $^1O_2$ and (2) chemical interaction to give a peroxy-oxy radical

Table 14. QUANTUM YIELDS FOR PHOTOLYSIS OF KETONES AT 25°C: STRUCTURE AND SOLVENT EFFECTS

Ketone	Solvent[a]	ϕ[b]	Reference
Ketone: α-Cleavage			
Me_2CO	Or	0.001	c
Me_2CO	V	0.1	c
MeCO-t-Bu	Or	0.52	c
Cyclopentanone	Or	∿ 0.2	c
2,2-Dimethylcyclohexanone	Or	∿ 0.4	
PhCOt-Bu	Or	∿ 0.3	
$PhCOCH_2Ph$	Or	∿ 0.4	d
4-MeOPhCOt-Bu	Or	∿ 0.1	d
4-PhPhCOt-Bu	Or	< 0.001	d
Ketone: β-Cleavage			
$PhCO(CH_2)_2Me$	Or	0.36	e
$PhCO(CH_2)_2Me$	Al	1.0	e
$PhCOCHMe_2$	Or	0.36	d
$PhCO(CH_2)_2$-i-Pr	Or	0.25	d
$PhCO(CH_2)CH(Me)OMe$	Or	0.21	d
$PhCO(CH_2)_3CO_2Me$	Or	0.46	d
$XPhCO(CH_2)_3Me$	Or		d
X = H	Or	0.33	
X = p-MeO	Or	0.10	
X = m-MeO	Or	0.014	
X = p-Me	Or	0.29	

[a] Or = nonpolar organic solvent, V = vapor phase, Al = alcohol.

[b] Quantum yield in deaerated system.

(1) $$PhC(O\bullet)R + {}^3O_2 \longrightarrow PhC(O)R + {}^1O_2 \text{ or } {}^3O_2$$

(2) $$PhC(O\bullet)R + O_2 \longrightarrow PhC(O\bullet)R \quad (OO\bullet)$$

Quenching by oxygen typically is diffusion controlled k_q ($\sim 10^9$-10^{10} M^{-1} s^{-1}) and occurs with both singlet and triplet excited states. At one atmosphere of air, quenching will limit the lifetime of triplets to $< 10^{-3}$ sec (Turro , 1978). Unless some other fast intramolecular process intervenes, oxygen quenching will significantly reduce the value of ϕ. Kinetic analysis indicates that quenching or reaction of ketone biradicals with oxygen will not compete with cleavage, cyclization, or reversion to ketone. Quenching of the precursor triplet species may be significant, however. Singlet oxygen, formed in the quenching process, may react further with ground state molecules and thereby lead to photosensitized oxygenation.

Reaction of oxygen to form bonds with excited species is also important and may serve either to quench the excited species or to form new products. Acetone reacts with O_2 to exchange oxygen, but cyclic ketones are reported to cleave to new oxygenated products (Baltrop and Coyle, 1975). Oxygen can also react with carbon radicals to trap them and thereby minimize recombination and dramatically increase Φ.

$$R\text{-}X \rightleftharpoons R\bullet + X\bullet$$

$$R\bullet + O_2 \longrightarrow RO_2\bullet$$

Aromatic rings exhibit a remarkable variety of photoprocesses including coupling, rearrangement, contraction of expansion, and oxidation (Barltrop and Coyle, 1975). Photolyses of several aromatic chemicals in aerated water show no specific pattern of quantum yields, dependence on oxygen concentration, or product formation (Smith et al., 1978). Indeed the frequent citation of photooxidations of polyaromatics to form endoperoxides or quinones may prove to be exceptions to the general reaction patterns of these chemicals. Quantum yields for several aromatics photolyzed in aerated or deaerated water are listed in Table 15. In summary, detailed SRC for quantum yields are not available at this time and a great deal of additional work is needed to provide the theoretical and empirical foundation needed for their development.

Oxidation Processes

Oxidation is a major loss process in the environment where significant concentrations of oxidants are generated by photochemical processes involving natural and anthropogenic light absorbers. In urban atmospheres, both HO• radical and O_3 are generated by a complex photocycle involving NO_2, O_2, and organic pollutants. In natural water, RO_2• radical and singlet O_2 ($^1O_2$) are generated by photolysis of humic materials dissolved or suspended in water.

Direct photooxidation of many molecules also occurs by way of excited

Table 15. QUANTUM YIELDS OF SELECTED PROCESSES IN THE PRESENCE AND ABSENCE OF OXYGEN IN WATER[a,b]

Chemical	Oxygen	ϕ[c]
Benzanthracene	Present	3.3(-3)
	Absent	< 3(-3)
Benzpyrene	Present	8.9(-4)
	Absent	∿ 0
Benzquinoline	Present	1.4(-2)
	Absent	< 1(-2)
9-H-carbazole	Present	7.6(-3)
	Absent	7.6(-3)
Dibenzcarbazole	Present	2.8(-3)
	Absent	2.8(-3)

[a]Solutions in oxygenated or argonated water.

[b]Unpublished data of Mill et al. (1979).

[c]Numbers in parentheses are powers of ten.

state interactions with triplet O_2, but the rates of these processes are controlled by the photophysics and photochemistry of excited states, not by the thermal chemistry of oxidant-molecule interaction (see Photochemistry section).

Recent reviews of oxidation in water and in air (Mill et al., 1979; Hendry and Kenley, 1979) suggest that only a few selected oxidants are probably important in either air or water. Table 16 lists these oxidants and their average diurnal concentrations.

Table 16. OXIDANT CONCENTRATIONS IN WATER AND AIR

Oxidant	Concentration, M
	Water[a]
$RO_2\bullet$	1×10^{-9}
$^1O_2$	1×10^{-12}
	Air[b]
$HO\bullet$	3.4×10^{-15}
	(8.2×10^{-8} ppm)
O_3	1.7×10^{-9}
	(4.1×10^{-2} ppm)

[a]From Mill et al. (1978).
[b]From Hendry et al. (1979).

SRC For Oxidation

The concentrations and known reactivities of the major oxidants provide a simple basis on which to separate reactive and nonreactive classes of chemicals in oxidations in air or water. Those classes of chemicals that have half-lives of more than one year may be considered as inert to these chemical oxidants and thus can be excluded from screening tests for oxidation. Tables 17-20 list half-lives for a variety of organic structures in reactions with $RO_2\bullet$, $^1O_2$, $HO\bullet$, and O_3, based on the reasonable assumption that the rate of a specific oxidation process follows the relation

$$-d[C]/dt = -k_{OX}[OX][C] \qquad (22)$$

TABLE 17 RATES OF OXIDATION BY $RO_2\bullet$ RADICAL IN SOLVENTS AT 30°C

Class	k_p[a] $M^{-1} s^{-1}$	Half-Life, $t_{1/2}$[b] days
Hydrocarbons	0.01	8×10^5
Olefin	0.09	9×10^4
Benzyl	1	8×10^3
Aldehyde	0.1	8×10^4
Alcohol	0.01	8×10^5
Phenol	1×10^4	0.8
Aromatic amine	1×10^4	0.8
Hydroquinone	1×10^6	12 min
Hydroxylamine	1×10^5	120 min
Hydroperoxide	1×10^5	120 min
Polycyclic aromatic	1×10^3	8

[a]Per reactive X-H bond ; from Hendry et al. (1974) and Howard (1972).

[b]For 1×10^{-9} M RO_2; $t_{1/2} = \ell n\ 2/8.64 \times 10^{-5}$ kp in days.

TABLE 18 RATES OF OXIDATION BY SINGLET OXYGEN IN SOLVENTS AT 25°C

Class	$k_{^1O_2}$[a] M^{-1} s^{-1}	Half-Life[b], $t_{1/2}$
Alkanes	< 2×10^2	> 100 yrs
Alcohols and ethers	< 2×10^2	> 100 yrs
Ketones and Aldehydes	< 2×10^2	> 100 yrs
Aromatics (including amines and phenols)	< 2×10^2	> 100 yrs
Alkyl halides	< 2×10^2	> 100 yrs
Acids and esters	< 2×10^2	> 100 yrs
Unsubstituted olefin	3×10^3	7.3 yrs
Cyclic olefins	2×10^5	40 days
Substituted olefin	1×10^6	8.0 days
Dialkyl sulfide	7×10^6	27 hrs
Diene	1×10^7	19 hrs
Imidazoles	4×10^7	4.8 hrs
Furans	1.4×10^8	1.0 hrs
Trialkyleneamines	8×10^8	14 mins

[a]Per molecule from Foote (1975) and Mill et al. (1979).

[b]For 1×10^{-12} M $^1O_2$; $t_{1/2} = \ln 2/k_{^1O_2} \times 10^{-12}$ in sec.

TABLE 19. RATE CONSTANTS FOR OXIDATION BY HO• RADICAL IN THE ATMOSPHERE AT 25°C.[a]

Class	10^{-9} k_{HO} M^{-1} s^{-1}	$t_{1/2}$[b] Days
n-Alkanes (C_3 - C_8)	1.3-5.0	1.3-4.3
iso-Alkanes (C_4 - C_{10})	0.6-2.9	1.9-9.4
Cycloalkanes (C_4 - C_8)	0.7-4.1	1.4-8
Halomethanes (1-3 fluorines or chlorines)	1.2(-4) - 0.065	87-47,000
Haloethanes (1-3 chlorines and 3-4 fluorines)	6(-3)-0.23	24-950
Butanone	1.9	2.9
p-Alcohols (C_2 - C_3)	2	2.8
sec-Alcohols (C_3 - C_4)	4.1	1.3
Ethers (C_2 - C_8)	2.5-1.0	0.6-2.2
Terminal olefins (C_2 - C_7)	4.6-34	0.2-1.2
Internal olefins (C_2 - C_3)	29-90	0.06-0.2
Aromatics		
benzene	0.82	6.8
toluene	3.5	1.6
xylenes	5.9-12	0.47-1.0
Trimethylbenzenes	15-30	0.2-0.4
Ethylbenzene	4.4	1.3
Propylbenzene	3.5	1.6
Cumene	4.6	1.2
o-Cresol	20	0.3
Benzaldehyde	7.6	0.74

[a]From Hendry and Kenley (1979).

[b]Assumes [HO•] is 3.4×10^{-15} M and 10 hrs solar days: $t_{1/2} = 0.69/k(3.4 \times 10^{-15}) \times (3600) \times (10)$.

TABLE 20 RATES OF OXIDATION BY OZONE IN THE ATMOSPHERE AT 25°C[a]

Class	k_{O_3}[b] M^{-1} s^{-1}	Half-Life, $t_{1/2}$ days[c]
Alkanes	< 0.005	> 2 (6)
Terminal Olefins	5.8 (3)	1.4
Internal Olefins	110 (3)	0.7
Branched Internal Olefins	(300-900) (3)	0.2-0.6 hr
Chloroethylenes	< 60	> 130
Alkylaromatics	< 60	> 130
Alkynes	< 60	> 130

[a]From Hendry and Kenley (1979).

[b]Per molecule.

[c]Based on 1 x 10^{-9} M O_3; $t_{1/2}$ = ℓn/8.6 x 10^{-5} k_{O_3} in days.

If [OX] is constant* equation (21) becomes

$$-d[C]/dt = -k'_{OX}[C] \quad (23)$$

and the half-life for chemical C is

$$t_{\frac{1}{2}} = \ell n2/k'_{OX} \quad (24)$$

Oxidation by $RO_2\bullet$

The range of measurable reactivities of organic compounds towards $RO_2\bullet$ radicals covers about 10^{10} in k_{OX} [Howard, 1972)]. Only chemicals that react with rate constants > 10^3 M^{-1} s^{-1} will be oxidized in aquatic systems at significant rates (Table 17). Therefore, we can exclude from testing any compound that has only CH or aromatic structures and all of their simple derivatives including carbonyls, esters, alcohols, halides, aliphatic amines, and ethers.

Aromatic amines and phenols are two major classes of chemicals that are reactive enough toward $RO_2\bullet$ radical to warrant detailed consideration regarding SRC. Fortunately, because these compounds are useful as antioxidants, several investigators have measured absolute rate constants for H-atom transfer to $RO_2\bullet$ from many types of phenols and some amines (Howard and Ingold, 1963; Howard, 1973).

$$RO_2\bullet + XPhOH \xrightarrow{k_{inh}} RO_2H + XPhO\bullet$$

Table 21 summarizes the absolute rate constants (k_{inh}) for selected classes of phenols; values of ρ^+ for each subseries of phenols are also listed. In all cases ρ^+ is negative, indicating that the transition state has some positive character stabilized by electron donor substituents. The reactivity of all measured phenols ranges from a low of about 3×10^2 M^{-1} s^{-1} for 4-CNPhOH to a high of about 9×10^4 M^{-1} s^{-1} for k_{inh} for hydroquinone extrapolated to the same temperature. Aromatic amines have been subject to less systematic study than phenols; nonetheless, the data listed in Table 22 shows that as a group, amines are as reactive or more so than phenols: values of k_{inh} range from a low of 9×10^2 M^{-1} s^{-1} for $MeO_2CPhNHMe$ to highs of 2×10^5 M^{-1} s^{-1} for diphenylamines. Values of ρ are negative and are similar to those for phenols (-0.8 to 0.6).

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*This assumption is usually referred to as a steady-state assumption and values used for [OX] take into account the fact that oxidants depend on sunlight and thus change in concentration diurnally.

TABLE 21. SRC FOR OXIDATION OF PHENOLS BY $RO_2\bullet$ RADICAL IN SOLVENTS

Substituent X	$10^{-4}\ k_{inh}\ M^{-1}\ s^{-1}$
XPhOH at 65°C with polystyrylperoxy radical[a]	
4-HO	9.3
4-Me	0.92
H	0.23
3-Cl	0.056
4-CN	0.030
$\rho^+ = -1.49$ in styrene	
$\rho^+ = -3.7$ in chlorobenzene	
$\rho^+ = -3.48 \pm 0.114$ in methyl methacrylate	
2,4-(t-Bu)$_2$-4-X-PhOH at -37°C with t-BuO•[b]	
MeO	2.3
Me	0.50
H	0.34
Cl	0.50
CN	0.10
$\rho^+ = -1.00$, r = 0.94 in isopentane	
o-Alkyl PhOH at 65°C with polystyryl peroxy radical[c]	
2,6-Me$_2$-4-XPhOH	
Me	2.8
Cl	1.2
CN	0.73
H	0.89
$\rho^+ = -1.36 \pm -1.46 \pm 0.115$	

TABLE 21 (Concluded)

Substituent X	$10^{-4} k_{inh}$ $M^{-1} s^{-1}$
2-t-Bu-n-XPhOH	
H	0.75
4-MeO	10.7
5-Me	1.1
4-IN	0.087
$\rho^+ = -1.46 \pm 0.012$	
2,6-(t-Bu)$_2$-4-XPhOH	
H	0.23
MeO	3.1
Me	0.80
Cl	0.32
CN	0.077
NO_2	$\sim$ 0.05
$\rho^+ = -1.11 \pm 0.026$	

[a]Howard and Ingold, 1963a.
[b]Howard and Furimsky, 1973.
[c]Howard and Ingold, 1963b.

TABLE 22 SRC FOR OXIDATION OF AMINES BY $RO_2\bullet$ RADICAL IN SOLVENTS

Amine	$10^{-4}\ k_{inh}\ M^{-1}\ s^{-1}$
N-Methylanilines at 65°[a,b]	
4-H	0.4
4-Me	1.2
3-Me	0.5
4-MeOC(O)	0.09
4-MeO	1.9
$\rho = -1.6$	
Diphenylamines at 65°[a,b]	
4,4′-H_2	4
4,4′-Me_2	10
4,4′-$(MeO)_2$	33
4,4′-$(NO_2)_2$	0.16
4-MeO	20
3-Cl	1.8
4-NO_2	0.6
$\rho^+ = -0.89$	
Napthylamines at 40°C[a,b]	
N-α-Napthyl	0.15
N-α-Naphthyl-N-Phenyl	1.25
N-β-Napthyl-N-Phenyl	10
N,N-Di-β-Napthyl	18

a In reaction with poly(peroxystyryl)peroxy radical.
b From Brownlie and Ingold (1967).

All these data were measured in nonpolar organic solvents. No useful data are available to indicate the extent of solvent effects on the process, for use in extrapolating to water; however, Ingold and Howard (1963) have speculated that ρ may increase with an increase in the solvent polarizability. For the present we probably can use the relative values of k_{inh} for phenols and amines with few reservations, but the absolute values in water may prove to be different from those in organic solvents.

Oxidation by Singlet Oxygen ($^1O_2$)

Zepp et al. (1978) demonstrated that sunlight irradiation of natural waters led to production of $^1O_2$ at average concentrations of 1×10^{-12} M. This value when combined with rate constants for oxidation a variety of organic structures (Table 18) lead to predictions of very long half-lives for most simple structures. Reactive molecules that warrant laboratory testing are electron-rich molecules such as branched olefins, eneamines, polycyclic aromatics, and sulfides.

Estimation Methods

SRC for $^1O_2$ oxidations are very limited. Foote and Denny (1971) measured the relative rates of oxidation of a series of substituted styrenes and found that for allylic oxidation correlation by the Hammett equation (σ) was satisfactory and $\rho = -0.92$. However, epoxidation of the styrene double bond which accompanies allylic oxidation is not correlated well by σ nor σ^+, but is correlated by $[\sigma - 0.37\ (\sigma^+ - \sigma)]$ to give $\rho = -0.87$.

Oxidation by HO• Radical

HO• radical is the most important oxidant in the atmosphere. It reacts by H-atom transfer and addition to double bonds and aromatic rings. Table 19 lists rate constants for reaction of HO• radical with a variety of organic structures. More detailed lists of rate constants are found in Hendry and Kenley (1979) and Hampson and Garvin (1977). Most organic molecules with -CH- or $-CH_2-$ bonds or aromatic, react rapidly with half-lives of less than a day; highly halogenated chemicals including, of course, Freons are much less reactive or unreactive.

Estimation Methods

The rate constant k_{HO} for oxidation of a specific structure can be estimated using the additivity procedure of Hendry and Kenley (1979) which, depending on the structure, requires estimation of the individual rate constants for H-atom transfer and addition. The expression for H-atom transfer is

$$k_{HO(H)} = \Sigma n_i \alpha_i \beta_i k_i \qquad (25)$$

in which α_i and β_i are substituent constants and k_i is the rate constant for the i-th CH bond. Similar expressions have been developed for addition to double bonds and to aromatic rings. The probable error in values of k_{HO} estimated in this way is about a factor of two (± 100%). A listing of substituent constants is found in the report by Hendry and Kenley (1979).

Oxidations by Ozone

Ozone is a selective oxidant that reacts only with electron-rich molecules such as olefins, eneamines, some phenols and polycyclic aromatics. Rate constants summarized in Table 20 show that of the structures listed only branched alkenes react fast enough with ozone for this reaction to compete with oxidation by HO• radical. A useful summary of specific rate constants for ozone oxidations in the gas-phase is found in Hendry and Kenleys' report (1979).

Estimation Methods

Huie and Herron (1974) were able to correlate rate constants, k_{O_3}, for gas-phase oxidations with ionization potentials for olefins. As expected the value of k_{O_3} increases with increasing ease of ionization. We are aware of no other SRC for ozone reactions in the atmosphere.

Physical Transport

Two major transport processes which can control environmental concentrations of chemicals in specific locations are sorbtion to sediment or soil and volatilization from water, air. Movement in soil, run-off, leaching to water and bioconcentration in organisms are beyond the scope of this report.

Volatilization

Theory and Measurement

Volatilization of chemicals from water to air is now recognized as an important transport process for a number of chemicals that have low solubility and low polarity; volatilization from surfaces is also a major transport process for many chemicals deliberately applied to fields. Despite very low vapor pressure, many chemicals can volatilize at surprisingly rapid rates owing to their very high activity coefficients in solution.

Mathematical expressions for the rate of volatilization from water, have been developed by Liss and Slater (1974) and MacKay and Leinonen (1975). The rate constant for volatilization from water (k_{vw}) is given by the relation

$$k_{vw} = \frac{A}{V}\left[\frac{1}{K_L} + \frac{RT}{H_c K_G}\right]^{-1} \qquad (25)$$

where

A = Surface area (cm^2)
V = Liquid volume (cm^3)
H_c = Henry's law constant (torr M^{-1})
K_L = Liquid film mass transfer coefficient ($cm\ hr^{-1}$)
K_G = Gas film mass transfer coefficient ($cm\ hr^{-1}$)

R = Gas constant (torr $°K^{-1}$ M^{-1})
T = Temperature (°K)

Mackay and Wolkoff (1973) showed that an estimate of H_c can be obtained from

$$H_c = P_{sat}/[C]_{sat} \tag{27}$$

where P_{sat} is the vapor pressure of pure chemical (or the hypothetical super-cooled liquid, if S is a solid) and $[C]_{sat}$ is the solubility of C in S (mol $liter^{-1}$). Equation (26) simplifies if $H_c > 1000$

$$k_{vw} = \frac{AK_L}{V} \tag{28}$$

where mass transfer is liquid-phase limited; if $H_c << 1000$ then equation becomes

$$k_{vw} = \frac{A}{V} H_C K_G (RT)^{-1} \tag{29}$$

and the process becomes limited by gas phase mass transfer.

For high volatility compounds a simple relative measurement for volatility becomes possible because the rate constant for volatilization of the chemical is proportional to the rate constant for volatilization or re-aeration of oxygen from the same solution over a range of turbulence

$$\frac{k_{vw}^{C}}{k_{vw}^{O_2}} = n \tag{30}$$

If the value of $k_{vw}^{O_2}$ in a real water body is known then

$$k_{vw}^{C}(\text{water body}) = nk_{vw}^{O_2}\ \text{water body} \tag{31}$$

Spencer et al. have reviewed volatilization processes from soil surfaces (1973). The overall process is complicated by variable contributions from volatilization of the chemical from the water at the surface, evaporation of water itself and the wick effect that brings more water and dissolved chemical to the surface. Initially volatilization of the chemical from the surface water will be rate controlling and equation (26) can be used to estimate the rate constant. This model will fail as a concentration gradient of chemical is established through the soil column and at this time no simple laboratory measurement will reliably measure the process in a way that can be extrapolated to the field.

Predictive Methods

Smith et al. (1978) have shown that for chemicals with H_C > 1000 torr M^{-1} a reasonably good estimate of the ratio $k_{vw}^{C}/k_{vw}^{O_2}$ can be made from the relation between the ratio of volatilization rate constants and the ratio of molecular diameters for O_2 and the chemical

$$\frac{k_{vw}^{C}}{k_{vw}^{O_2}} = \frac{D^{O_2}}{D^{C}} \tag{32}$$

For chemicals having H_C < 1000 torr M^{-1} no satisfactory estimation provedure is available.

Values of H_C can be estimated from equation (27) if both solubility and vapor pressure are known at temperatures close to 25°C. We know of no reliable SRC that might be used to estimate H_C or solubility.

Sorption to Sediment and Soil

Measurement Procedures

Sediments and soils are complex mixtures of alumino-silicate minerals (clays), metal oxides, water and humic materials. The proportions of these components will vary widely from one source to another as will the particle size distribution.

Many organic chemicals especially those that are nonpolar and insoluble in water, sorb strongly to sediments or soils. If the fraction of chemical sorbed to sediment or soil is large, the overall loss rate of chemical by other transformation processes will be slowed; in effect, sorption serves to buffer the concentration of chemical present in the aqueous phase [see equation (12)]. In some cases reversible sorption to sediments or soils may be followed by irreversible transformation of the chemical in the sorbed state such as reduction of carbon-halogen bonds (Williams and Bidleman, 1978). Possibly other transformations may occur as well.

The equilibrium ratio of sorbed to non-sorbed chemical on a sediment may be expressed as an equilibrium constant (constant temperature)

$$K_s = [C]_s/[C]_w \tag{33}$$

The concentrations of C in sediment or soil are in μg ml^{-1}; for water 1 ml = 1 g, and K_s becomes dimensionless. Strongly sorbed chemicals such as benzo[a]pyrene or mirex have $K_s > 10^5$ and weakly sorbed chemicals such as nitroaromatics or quinoline have $K_s < 10^2$.

Values of K_s for a single chemical will vary with the composition of the sediment. To place sediments in a more nearly equal basis the value K_s can be expressed as

$$K_s = AK_{sc} \tag{34}$$

where A is the fraction of organic content expressed as mg C per mg sediment; thus K_{sc} is a sorption constant corrected for the organic content. It follows from equation (34) that if a = 1 then K_s is equivalent to a partition coefficient such as the octanol-water coefficient (K_{ow}).

Predictive Methods

Recent studies and correlations by Karickoff et al. (1978) and by Kanaga and Goring (1978) bring out the close direct relationship between K_{sc} solubility, bioconcentration and the organic content of the sediment or soil. Other studies notably by Chiou (1977) have shown a similar relationship between K_{ow} and solubility such that

$$\log K_{ow} = n \log(\text{solubility}) + c \qquad (35)$$

Smith and Bomberger (1979) have taken the data of Karickoff et al., Kanaga and Goring, and Smith et al. (1978), rescaled the data to one coordinate set, and developed the following regression relation

$$\log K_{sc} = -0.782 \log[C] - 0.27 \qquad (36)$$

[C] is solubility in M

Figure 1 shows the combined data plotted as log K_{oc} (or K_{sc}) versus log (solubility) and the regression line. Using equation (36) and the solubility of the chemical in water the investigator can estimated K_{sc} within a power of ten for most non-polar chemicals - an accuracy sufficient in most cases, for screening purposes.

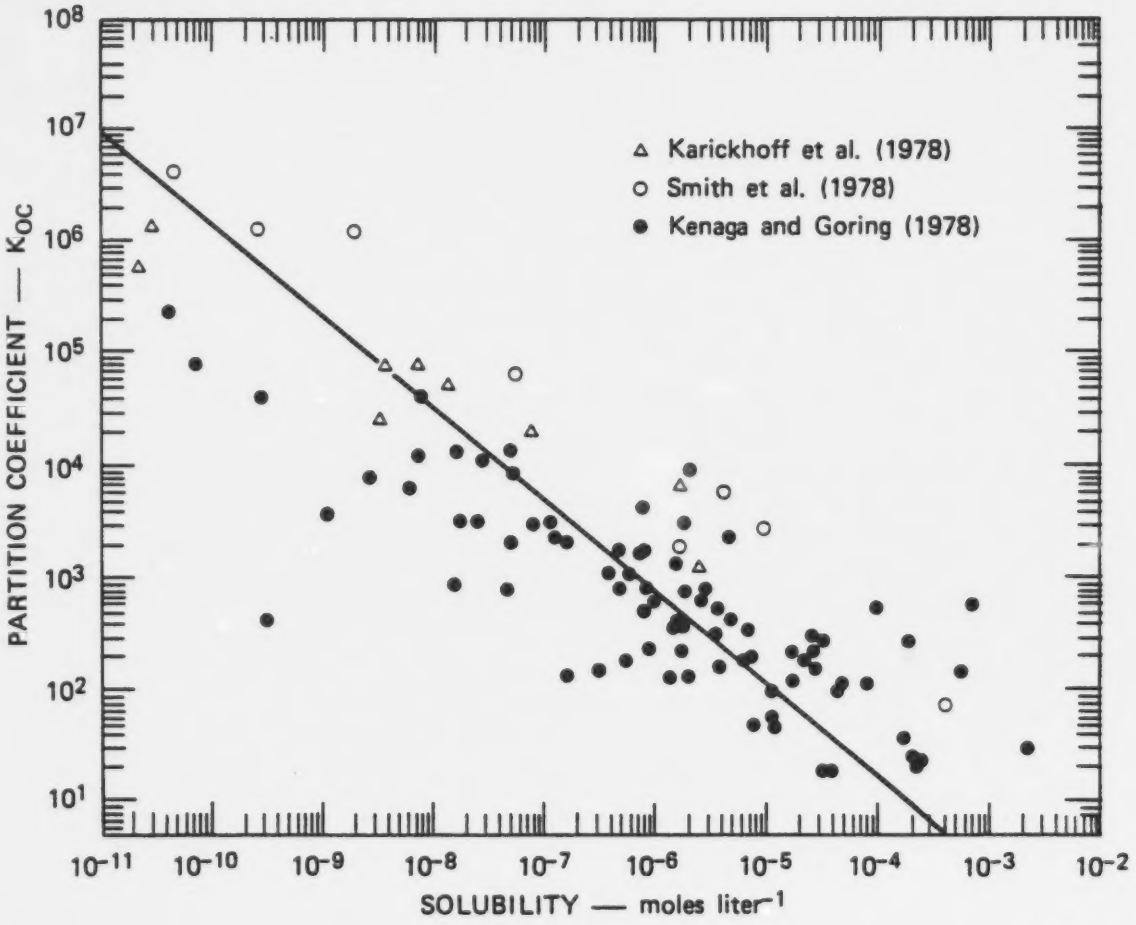

Figure 1. Soil or Sediment Partition Coefficient of Chemicals Versus Solubility in Water (Smith and Bomberger, 1979).

SECTION 4

METHODOLOGY FOR FATE ESTIMATION

The following calculational procedure illustrates how a specific chemical structure may be dissected into molecular fragments from which estimates of rate or equilibrium constants for each environmental process may be made. Fictitious physical property data are supplied to illustrate the use of the methods.

Example: 2-n-Butylcarboxy-5-hydroxynapthalene, $5\text{-HOC}_{10}\text{H}_6\text{-2-C(O)O-n-Bu}$

Solubility: 6×10^{-6} M at 25° (FICTITIOUS)
Vapor Pressure: 8×10^{-4} torr at 25° (FICTITIOUS)
uv Spectrum: 200-360 nm (FICTITIOUS)

Step 1. Calculation of Rate Constants for Chemical Transformation.

a. Hydrolysis - the ester function, n-butylcarboxy, will hydrolyze. Table 4 shows that esters of the type ArC(O)OAl will hydrolyze at pH 7 and 25,C with half-lives > 1 yr. More detailed examination of data in Mabey and Mill (1978) shows that these esters have a dominant base-catalyzed reaction, down to pH 4.5, and that although no napthyl esters are listed, the lifetimes for simple aromatic esters is long enough at pH 7 to make lifetimes at pH 9 3-6 months or longer.

b. Photolysis - the uv spectrum shows that the chemical will absorb in the solar region. The detailed spectrum taken in 50% acetonitrile/water (v/v) (not shown) is tabulated using the intervals proposed by Mabey et al. (1979) for solution photochemistry.

UV Spectrum of Napthylester (FICTITIOUS)

Interval Center, nm	Interval Range nm	Absorption Coefficient $M^{-1}\ cm^{-1}$
299	296.3-301.3	160
304	301.3-306.3	102
309	306.3-311.3	57
314	311.3-316.3	32
319	316.3-321.3	13
323	321.3-325.0	3
340	325.0-355.0	0.7
370	355-385.0	0

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Spectral data are now combined with sunlight intensity data for summer season over the same spectral range in equation (20) to calculate a maximum value of k_p. Intensity data are taken from Table 3.2, Mabey et al. (1979).

Solar Intensity, Summer

Interval Center, nm	Intensity, L_λ[a] einsteins cm^{-2} day^{-1}
299	4.4(-4)
304	3.2(-3)
309	9.6(-3)
314	2.0(-2)
319	3.0(-2)
323	3.0(-2)
340	3.5(-1)

[a]Rounded off to 2 places.

Since

$$k_p = \phi \Sigma \varepsilon_\lambda L_\lambda \qquad (20)$$

we assign a value of $\phi = 1$ and combine the ε_λ and L_λ data to give

$$k_p = 2.3 \text{ day}^{-1}$$

$$t_{1/2} = 0.3 \text{ day (for } \phi = 1)$$

A similar procedure could be carried out for photolysis in the atmosphere but because the result would be similar - intensity data and intervals are slightly different (Hendry et al., 1979) - there is no need to calculate both results in the zero level screening procedure.

c. Oxidation - oxidation in water may be an important fate for this chemical since it has a phenolic structure. Tables 17 and 21 show that α-naphthol has k_{RO_2} of $\sim 10^5$ M^{-1} s^{-1}. The effect of a C(O)OR group in the α-position in napthalene on the reactivity of a OH group in the 5-position is to deactivate it but the magnitude of the effect is uncertain. If we assume that reactivity in the napthalene series follows that in benzene then a C(O)OR group will slow the rate by $\sim$ 3x (Table 21) and $k_{RO_2} \cong 3 \times 10^4$ M^{-1} s^{-1}. The half-life of the chemical is then calculated by assuming that the average concentration of $RO_2\cdot$ in water is 1×10^{-9} M (Mill et al., 1979).

$$t_{1/2} = \ln 2/(3 \times 10^4) \times (1 \times 10^{-9})$$

$$= 2.3 \times 10^4 \text{ seconds}$$

$$= 6.4 \text{ hrs.}$$

Oxidation by $^1O_2$ will not be important for this chemical (Table 18, $t_{1/2}$ > 100 yrs). Oxidation by HO• radical in the atmosphere will be important since aromatics react with $k_{HO} > 1 \times 10^9\ M^{-1}\ s^{-1}$ (Table 19) and phenols are generally more reactive. The half-life in the atmosphere can be calculated by assuming that the average concentration of HO• in air is 3×10^{-15} M (Hendry et al., 1979).

$$t_{1/2} = \ln 2/(> 1 \times 10^9) \times (3 \times 10^{-15})$$

$$< 2.3 \times 10^5 \text{ sec}$$

$$< 64 \text{ hrs}$$

$$< 6.4 \text{ days as 10-hr solar days}$$

Oxidation by ozone will not be an important competing process for this chemical (Table 20).

Step 2 - Calculation of Rate or Equilibrium Constants for Physical Transformation

a. Volatility - the approximate method for estimating H_c from equation (27) gives

$$H_c = \frac{8 \times 10^{-4} \text{ torr}}{6 \times 10^{-6} \text{ M}}$$

$$= 130 \text{ torr } M^{-1} \text{ at } 25°C$$

This value of H_c, lying between 10 and 1000 torr M^{-1}, cannot be used to clearly exclude volatilization as an important process. Testing is needed.

b. Sorption to sediment - solubility data and the regression equation (36) are used to calculate a value of K_{sc}

$$\log K_{sc} = -0.782 \log[6 \times 10^{-6}] - 0.27$$

$$= 3.8$$

$$K_{sc} = 6.5 \times 10^3$$

Step 3 - Summary of Estimated Rate Constants

a. Chemical transformations

Process	$t_{1/2}$
Hydrolysis	
pH 5, 7	> 1 yr
pH 9	3-6 months

Photolysis (ϕ=1) (air or water)	0.3 day
Oxidation	
water ($RO_2\bullet$)	6 hrs
air ($HO\bullet$)	< 6 days
$^1O_2$ or O_3	> 10 yrs

b. Physical transport

Volatilization H_c	130
Sorption K_{sc}	6×10^3

The results of zero-level screening indicate that 2 n-butylcarboxy-5-hydroxy naphthalene may photolyze, oxidize and hydrolyze in water rapidly enough to warrant laboratory screening tests for sunlight photolysis in air and water, oxidation by $RO_2\bullet$ radical and $HO\bullet$ radical and hydrolysis at pH 9. No tests would appear to be needed for hydrolysis at pH 5 or 7 or oxidation by $^1O_2$ or O_3. Calculated values of H_c and K_{sc} indicate a need for screening measurements to evaluate volatility and sorption.

A decision to carry out oxidation and photolysis both in air and water would depend on whether volatilization measurements indicated the probable importance of movement from air to water to air. If the volatilization half-life were more than ten times longer than half-lives for transformations in water, probably no tests in air would be needed.

The foregoing calculations illustrate the value of estimation methods for calculating important kinetic and thermodynamic constants prior to testing to eliminate some processes from the testing scheme. The example selected and its property data were deliberately chosen to maximize the number of possible processes the chemical might undergo. Had we selected instead 2-n-butylcarboxy-5-methoxynapthalene, reference to Table 17 would show that oxidation in water would be too slow to warrant testing but the rates of hydrolysis, photolysis and oxidation in air would be relatively unaffected. Probably the sorption and volatility would be more important since solubility would be lower and the vapor pressure higher.

SECTION 5

CONCLUSIONS AND RECOMMENDATIONS

From the foregoing discussions several conclusions and recommendations for action emerge:

- Many of the important physical and chemical processes in water and air are well-enough understood to allow quantitative estimation of rate or equilibrium constants for specific chemical structures (zero-level screening).

- Two kinds of SRC are useful for application to environmental processes: general SRC provide a sound and general basis for segregating many classes of structures into reactive and non-reactive classes. Zero-level screening of this kind does not require expertise only basic training in organic chemistry. LFER provide a more limited basis for calculating specific rate constants for some classes of chemicals in some reactions. Use of LFER requires mechanistic insight and probable expertise in physical-organic chemistry.

- Among the chemical reactions of importance in air or water, oxidation and hydrolysis have the broadest range of SRC available. More data are needed to develop LFER for oxidation by HO• radical, $^1O_2$, possibly O_3, and for hydrolysis by OH^- of selected classes of chemicals.

- Photochemistry is the most complex chemical process occuring in air or water; the need for more reliable information on effects of oxygen phase change and natural quenchers on quantum yields is evident as is the need for information on the importance of sensitized reactions involving natural organics in water.

- Quantum yield estimation methods based on empirical and theoretical relationships including SRC and LFER are almost non-existent and need to be developed for almost all classes of chemicals that absorb sunlight.

- Critical constants for transport processes can be estimated readily from solubility and vapor pressure data for a limited range of volatilities and solubilities. Reliable SRC for K_{oc} (K_{ow}) are now limited to non-ionic chemicals; comparable sorption SRC for ionic species are needed as is a larger data base. Quantitative relations are lacking between H_c and k_v for intermediate values of H_c ($> 10 < 1000$). These should be developed.

- No reliable kinetic data base is available for microbiological transformations from which SRC for these processes might be developed. Studies by Wolf et al. (1979) suggest a relation between chemical and

microbiological rate constants for hydrolysis. Additional studies of this kind should be performed.

- Transformations in soil and sediment are poorly understood. Only if more detailed studies are performed to characterize the chemical species involved in these processes will development of reliable SRC be possible. Needed studies include hydrolysis, oxidation, photolysis and reduction.

- SRC now available can be used in a systematic and objective manner for zero level screening; the methodology is an efficient and reliable technique for selecting out those laboratory screening tests needed for fate assessment thereby saving considerable time and money both for EPA and chemical manufacturers.

- Methodology for using SRC on zero level screening needs to be optimized and systemized in order that scientifically literate but inexperienced personnel can use these methods reliably. Eventually computerized decision-tree analysis programs should be developed but "hand" analysis using tabulated SRC data is also efficient and easily used.

- EPA should develop a comprehensive instruction manual for zero level screening. The manual will include a logic-key decision sequence to characterize possible important processes for a specific molecular structure and a detailed tabular listing of equations, environmental properties and rate constants for these processes. The decision sequence will be keyed to the tables and equations. If properly designed, non-expert personnel can use this manual for zero-level screening with a high degree of confidence.

REFERENCES

Baltrop, J. A., and J. D. Coyle. 1975. Excited States in Organic Chemistry. John Wiley and Sons, Inc. New York.

Benson, S. W. 1976. Thermochemical Kinetics, Second Edition. John Wiley, New York.

Bloch, S., F. Ravlin, A.Toupance, and R. Buvet. 1973. Etude de la decomposition du malodinitrile en solution aqueuse alkaline. Comp. Rendu, Acad. Sci. Paris 276:915.

Brownlie, I. T., and K. U. Ingold. 1967. The Inhibited Autoxidation of Styrene. Part VI. The Relative Efficiencies and the Kinetics for Inhibition by N-aryl Anilines and N-alkyl Anilines. Can. J. Chem. 45:2419.

Calvert, J. G., and J. N. Pitts. 1967. Photochemistry. John Wiley, New York.

Chapman , N. B., and J. Shorter. 1972. Advances in Linear Free Energy Relationships. Plenum Press, New York.

Chiou, G. T., B. H. Freed, D. W. Schmedding, and K. L. Kohnert. 1977. Partition Coefficients and Bioaccumulation of Selected Organic Chemicals. Environ. Sci. Technol. 11:475.

Euranto, E. K. 1969. Chemistry of Carboxylic Acid Esters. S. Patai, Ed. Interscience Publishers, New York, p. 505-588.

Exner, O. 1972. The Hammett Equation - the Present Position in Advances in Linear Free Energy Relationships. N. B. Chapman and J. Shorter, Eds. Plenum Press, New York. pp. 1-70.

Exner, O. 1975. Range, Validity, and Precision of Correlation Equations. Coll. Czech. Chem. Comm. 40:2781-9.

Federal Register. 1979. Toxic Substances Control: Discussion of Premanufacture Testing Policy and Technical Issues; Requests for Comments. March 16 Part IV, pp. 16240-16292.

Foote, C. S. 1976. Free Radicals in Biology. W. A. Pryor, ed. Academic Press, Inc., New York.

Foote, C. S., and R. W. Denny. 1971. Chemistry of Singlet Oxygen. XIII. Solvent Effects on the Reaction with Olefins. J. Am. Chem. Soc., 93:5168.

Hendry, D. G., T. Mill, L. Piszkiewicz, J. A. Howard, and H. K. Eigenmann. 1974. A Critical Review of H-Atom Transfer in the Liquid Phase. Chlorine Atom, Alkyl, Trichloromethyl, Alkoxy and Alkylperoxy Radicals. J. Phys. Chem. Ref. Data 3:937.

Hendry, D. G., T. Mill, and W. Mabey. 1979. Test Protocols for Environmental Processes: Oxidation and Photolysis in Air. EPA Report (Draft). EPA Contract 68-03-2227.

Hendry, D. G., and R. Kenley. 1979. Atmospheric Reaction products of Organic Compounds. EPA Final Report. EPA Contract 560/12-79-001.

Howard, J. A., and K. U. Ingold. 1963. The Inhibited Autoxidation of Styrene. Part II. Can. J. Chem. 41:1744.

Howard, J. A. 1972. Absolute Rate Constants for Reactions of Oxyl Radicals. Adv. Free Radical Chem. 4:49.

Howard, J. A., and E. Furimsky. 1973. Arrhenius Parameters for Reactions of tert-Butylperoxy Radicals with Some Hindered Phenols and Amines. Can. J. Chem. 51:3738-3745.

Hudsen, R. F., and J. F. Wardill. 1950. Mechanism of Hydrolysis of Acid Chlorides. Part I. J. Chem. Soc., 1729-1733.

Kanaga, E. E., and C.A.I. Goring. 1978. Relationship Between Water Solubility, Soil Sorption, Octanol-Water Partitioning and Bioconcentration of Chemicals in Biota. Preprint, Amer. Soc. Testing Materials, Third Aquatic Toxicology Symposium, New Orleans, Louisiana, October 17-18.

Karickoff, S. W., D. S. Brown, and T. A. Scott. 1978. Sorption of Hydrophobic Pollutants on Natural Sediments. EPA Internal Report, Environmental Research Laboratory, Athens, Georgia.

Kiniven, A. 1972. Chemistry of Acyl Halides. S. Patai, Ed. Interscience Publishers, New York.

Liss, P. G., and P. G. Slater. 1974. Flux of Gases Across the Air-Sea Interface. Nature 247:181.

Mabey, W. R., T. Mill, and D. G. Hendry. 1979. Test Protocols for Environmental Processes: Photolysis in Water. EPA Report (Draft). EPA Contract 68-03-2227.

Mabey, W. R., and T. Mill. 1978. Critical Review of Hydrolysis of Organic Compounds in Water Under Environmental Conditions. J. Phys. Chem. Ref. Data 7:383.

Mackay, D., and A. Wolkoff. 1973. Rate of Evaporation of Low-Solubility Contaminants from Water Bodies to Atmosphere. Environ. Sci. Technol. 7:611.

Mill, T. 1979. Data Needed to Predict Environmental Fate of Organic Compounds. Proceedings of Symposium on Environmental Fate held at meeting of Amer. Chem. Soc., Miami, FL, Sept. 1978. Ann Arbor Publishers, in press.

Mill, T., W. R. Mabey, and D. G. Hendry. 1979. Test Protocols for Environmental Processes: Oxidation in Water. EPA Report (Draft). EPA Contract 68-03-2227.

Perkampus, H. H., et al. 1971. UV Atlas of Organic Compounds. Vol. I-V. Plenum Press, New York.

Shorter, J. 1972. Advances in Linear Free Energy Relationships. N. B. Chapman and J. Shorter, Eds. Plenum Press, New York. p. 71.

Smith, J. H., W. R. Mabey, N. Bohonos, B. R. Holt, S. S. Lee, T.-W. Chou, D. C. Bomberger, and T. Mill. 1978. Environmental Pathways of Selected Chemicals in Freshwater Systems, Part I. EPA Report 600/7-77-113.

Smith, J. H., and D. Bomberger. 1979. Unpublished results.

Spanggord, R. J., T. Mill, T.-W. Chou, W. R. Mabey, J. H. Smith, and S. Lee. 1979. Environmental Fate Studies on Certain Munition Wastewater Constituents. Phase I Literature Review. Final Report U.S. Army Medical Bioengineering Research and Development Lab. Fort Detrick, MD.

Spencer, W. F., W. Farmer, and M. M. Cliath. 1973. Pesticide Volatilization. Residue Rev. 49:1.

Turro, N. J., V. Ramamurthy, W. Cherry, and W. Farneth. 1978. Effect of Wavelength on Organic Photoreactions in Solution. Chem. Rev. 78:125-144.

Wagner, P. J., and A. E. Kemppainen. 1968. Is There Any Correlation Between Quantum Yields and Triplet-State Reactivity in Type II Photoelimination? J. Am. Chem. Soc. 90:5896-97.

Wells, P. R. 1963. Linear Free Energy Relationships. Chem. Rev. 63:171.

Widequist, S. 1956. The Alkaline Hydrolysis of Acetonitrile. Arkiv. for Kemi. 10:256.

Williams, A. 1972. Alkaline Hydrolysis of Substituted Phenyl n-Phenylcarbamates. J. Chem. Soc. Perkin II. p. 808.

Williams, R. R., and T. F. Bidleman. 1978. Toxaphene Degradation in Estuarine Sediments. J. Agric. Food Chem. 26:280.

Wolfe, N. L., R. G. Zepp, and D. F. Paris. 1978. Use of Structure-Reactivity Relationships to Estimate Hydrolytic Persistence of Carbamate Pesticides. Water Res. 12:561.

Wolfe, N., et al. 1979. Unpublished results.

Zavoianu, D. 1968. Structure and Reactivity of Nitriles. An. Univ. Bucuresti, Ser. Stiint. Natur. Chim. 17:41-66.

Zepp, R. G., N. L. Wolfe, G. L. Baughman, and R. C. Hollis. 1978. Singlet Oxygen in Natural Water. Nature 278:421.

Zepp, R. G., and D. M. Cline. 1977. Rates of Direct Photolysis in Aquatic Environments. Environ. Sci. Technol. 11:359-366.